Advanced Concepts for Photovoltaic Cells

Arthur J. Nozik
Center for Basic Sciences
National Renewable Energy Laboratory
Golden, CO 80401

ABSTRACT

Novel approaches to high efficiency photovoltaic cells are discussed that are based on the use of semiconductor quantum dots to slow hot electron cooling and thus produce either enhanced photocurrents through impact ionization or enhanced photovoltages through hot electron transport and collection.

1. Introduction

Recent detailed analyses indicate that from 10 to 30 TW-yr of annual carbon-free energy (1 TW = 1 x 10^{12} watts; 1 TW-yr = 31.5 x 10^{18} joules = 31.5 EJ; 1 Quad = 10^{15} BTU = 1.055 EJ) will be required globally by the year 2050 to accommodate the world's expected population of 10-11 billion people, combined with a modest annual global economic growth rate of about 2 % (M.I.Hoffert, et al., *Nature* **395**, 881, 1998). The amount of carbon-free energy that will be needed depends upon the level of atmospheric CO_2 that can be tolerated with respect to its impact on global climate change. The present concentration of CO_2 is 275 ppm, up from 175 ppm before the industrial revolution. If CO_2 is to be stabilized at 750 ppm by 2050 (a level considered extremely dangerous and seriously disruptive by many climatologists), and if carbon sequestration is not considered, then about 10 TW-yr of annual carbon-free energy will be required by 2050. If the CO_2 level needs to be stabilized at 400 ppm, then 30 TW-yr of carbon-free energy will be required annually. The current global population is about 6 billion people and the total annual global energy consumption is about 13 TW-yr. Thus, enormous levels of carbon-free energy will have to be introduced in the coming decades—levels that are from 1 to 3 times the total level of energy consumed today from all sources (fossil fuel, nuclear power, and renewable energy)!

The solar constant is 1.76 x 10^5 TW; of this about 600 TW strikes the earth's terrestrial surfaces at practical sites suitable for solar energy harvesting. Solar energy is the largest renewable resource and at appropriate levels of cost and efficiency could provide the required levels of carbon-free energy.

The present cost (Generation I) based on single crystal Si is about $3.50/peak watt, yielding an energy cost of about $0.30 to 0.35 /kWhr. The grand future challenge for photovoltaics is to discover and develop PV systems that exhibit combinations of efficiency and capital cost per unit area that result in a cost of about $0.20/peak watt corresponding to delivered electrical energy of a few cents/kWhr. A cost level of $0.20/peak watt would make PV very attractive and lead to widespread application. Such a cost goal requires PV at $100/$m^2$ together with a conversion efficiency of about 45% or PV at $2/$m^2$ and an efficiency of 15 %. Such combinations of cost and efficiency require truly disruptive technologies that do not exist at the present time. However, the attainment of these goals does not conflict with nor violate any fundamental scientific principles and is theoretically feasible. Here we discuss one approach to the problem which could lead to ultra-high PV efficiencies with a single bandgap semiconductor.

2. Approach and Results

Our approach utilizes high energy electrons (termed hot electrons and created by absorption of solar photons larger than the bandgap) before these high energy electrons convert their excess kinetic energy (equal to the difference between the photogenerated electron energy and the conduction band energy) to heat through phonon emission. The formation of discrete quantized levels in semiconductor quantum dots affects the relaxation dynamics of high energy electrons and holes and could enhance the conversion efficiency by allowing electrical free energy to be extracted from the energetic electrons and/or holes before they relax to their lowest electronic state and produce heat.

As is well known, the maximum thermodynamic efficiency for the conversion of unconcentrated solar irradiance into electrical free energy in the radiative limit, assuming detailed balance, a single threshold absorber, and thermal equilibrium between electrons and phonons, was calculated by Shockley and Queisser in 1961 [1] to be about 31%. This efficiency is attainable in semiconductors with bandgaps ranging from about 1.25 to 1.45 eV.

However, the solar spectrum contains photons with energies ranging from about 0.5 to 3.5 eV. Photons with energies below the semiconductor bandgap are not absorbed, while those with energies above the bandgap create charge carriers with a total excess kinetic energy equal to the difference between the photon energy and the bandgap. This excess kinetic energy creates an effective temperature for an ensemble of photogenerated carriers that can be much higher than the lattice temperature; such carriers are called "hot electrons and hot holes", and their initial temperature upon photon absorption can be as high as 3000 K with the lattice temperature at 300 K.

In the Shockley-Queisser analysis, a major factor limiting the conversion efficiency to 31% is that the absorbed photon energy above the semiconductor bandgap is lost as heat through electron-phonon scattering and subsequent phonon emission, as the carriers relax to their respective band edges and equilibrate with the phonons. The main approach to reduce this loss and increase efficiency above the 31% limit

has been to use a stack of cascaded multiple p-n junctions in the absorber with bandgaps better matched to the solar spectrum. In the limit of an infinite stack of bandgaps perfectly matched to the solar spectrum, the ultimate conversion efficiency at one-sun intensity increases to about 66%. Other approaches to exceed the Shockley-Queisser limit include hot carrier solar cells [2-4], solar cells producing multiple electron-hole pairs per photon through impact ionization [5, 6], multiband and impurity solar cells [7, 8], and thermophotovoltaic/thermophotonic cells [7]. Here, we will only discuss hot carrier and impact ionization solar cells, and the effects of size quantization in semiconductor QDs on the carrier dynamics that control the probability of these processes.

There are two fundamental ways to utilize the hot carriers for enhancing the efficiency of photon conversion. One way produces an enhanced photovoltage, and the other way produces an enhanced photocurrent. The former requires that the carriers be extracted from the photoconverter before they cool [3, 4], while the latter requires the energetic hot carriers to produce a second (or more) electron-hole pair through impact ionization [5, 6]—a process that is the inverse of an Auger process whereby two electron-hole pairs recombine to produce a single highly energetic electron-hole pair. In order to achieve the former, the rates of photogenerated carrier separation, transport, and interfacial transfer across the semiconductor interface must all be fast compared to the rate of carrier cooling [4, 9, 10]. The latter requires that the rate of impact ionization (i.e., inverse Auger effect) is greater than the rate of carrier cooling and forward Auger processes.

In recent years, it has been proposed [4, 9, 11-14], and experimentally verified in some cases [2, 15-17], that the relaxation dynamics of photogenerated carriers may be markedly affected by quantization effects in the semiconductor (i.e., in semiconductor quantum wells, quantum wires, quantum dots, superlattices, and nanostructures). Specifically, the hot carrier cooling rates may be dramatically reduced, and the rate of impact ionization could become competitive with the rate of carrier cooling [2, 15] (see Fig. 1).

Equilibration of the hot carriers with the lattice is achieved through carrier–LO phonon interactions (LO phonon emission). The phonon emission results in cooling of the carriers and heating of the lattice until the carrier and lattice temperatures become equal.

However, in quantum dots, slowed hot electron cooling is theoretically possible by an effect called a "phonon bottleneck. Slowed cooling could make the rate of impact ionization (inverse Auger effect) an important process in QDs [2]. PL blinking in QDs (intermittent PL as a function of time) has been explained [18, 19] by an Auger process whereby if two electron-holes pairs are photogenerated in a QD, one pair recombines and transfers its recombination energy to one of the remaining charge carriers, ionizing it over the potential barrier at the surface into the surface region. This creates a charged QD that quenches radiative

emission after subsequent photon absorption; after some time, the ionized electron can return to the QD core and the PL is turned on again. Since this Auger process can occur in QDs, the inverse Auger process, whereby one high energy electron-hole pair (created from a photon with $hv > E_g$) can generate two electron-hole pairs, can also occur in QDs [2].

The first prediction of slowed cooling at low light intensities in quantized structures was made by Boudreaux, Williams and Nozik [4]. They anticipated that cooling of carriers would require multi-phonon processes when the quantized levels are separated in energy by more than phonon energies. They analyzed the expected slowed cooling time for hot holes at the surface of highly-doped n-type semiconductors, where quantized energy levels arise because of the narrow space charge layer (i.e., depletion layer) produced by the high doping level. For strongly
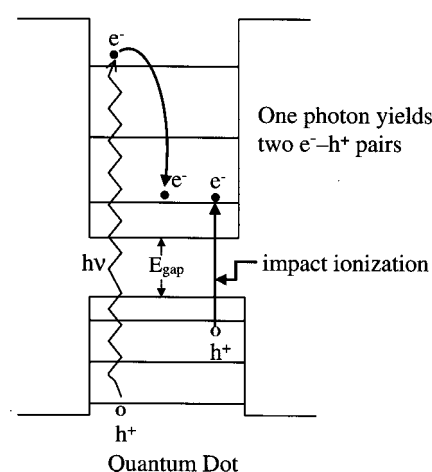

Figure 1. Enhanced photovoltaic efficiency in quantum dot solar cells by impact ionization (inverse Auger effect).

quantized electron levels, the hot electron cooling time could be > 100 ps.

More complete theoretical models for slowed cooling in QDs have been proposed by Bockelmann and co-workers [13, 20] and Benisty and co-workers [12, 14]. However, there are several other mechanisms by which hot electrons can cool in QDs. Most prominent among these is the Auger mechanism [21]. Here, the excess energy of the electron is transferred via an Auger process to the hole, which then cools rapidly because of its larger effective mass and smaller energy level spacing. Thus, an Auger mechanism for hot electron cooling can break the phonon bottleneck [21].

Over the past several years, many investigations have been published that explore hot electron cooling/relaxation dynamics in QDs and the issue of a phonon bottleneck in QDs. The results are controversial and there are many reports that both support and contradict the prediction of slowed hot electron cooling in QDs and the existence of a phonon bottleneck [2, 16, 17].
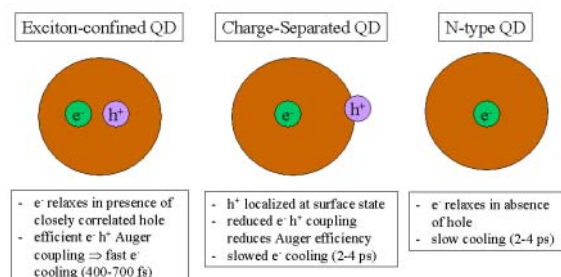

Figure 2. Different electron-hole configurations in a quantum dot and the resulting relaxation/cooling dynamics.

Studies of carrier cooling and relaxation have been performed on II-VI CdSe colloidal QDs by Klimov et al. [22, 23], Guyot-Sionnest et al. [24], Ellingson et al. [15, 17], and Blackburn et al. [16]. These results support the Auger mechanism for electron relaxation, whereby the excess electron energy is rapidly transferred to the hole which then relaxes rapidly through its dense spectrum of states. When the hole is rapidly removed and trapped at the QD surface, the Auger mechanism for hot electron relaxation is inhibited and the relaxation time increases.

Recently, results from NREL [16, 17] were reported for the electron cooling dynamics in InP QDs where the QD surface was modified to permit hole trapping but not electron trapping, and also where only electrons were injected into the QD from an external redox molecule (sodium biphenyl) so that holes necessary for the Auger cooling mechanism were not present in the QD [16]. If the electron and hole remain the QD core, strong electron-hole interaction leads to efficient, fast relaxation via the Auger mechanism, but in QDs, where the hole is localized at the surface, the increased spatial separation inhibits the Auger process and results in slower relaxation.

To further investigate the mechanisms involved in the intraband relaxation, experiments were conducted at NREL in which only electrons are present in the QDs. Sodium biphenyl is a very strong reducing agent which has been shown to successfully inject electrons into the conduction band of CdSe QDs [25, 26], effectively bleaching the 1S transition and allowing an IR-induced transition to the $1P_e$ level. Sodium biphenyl was therefore used to inject electrons into the 1S electron level in InP QDs [16]. This $1S_e$ electron may be excited to the $1P_e$ level with an IR pump and its relaxation dynamics back to the ground 1S state monitored. Time-resolved, IR-induced transitions in n-type (electron injected) InP QDs show that he relaxation of the excited electrons from the 1P to the 1S level can be fit to a single exponential, with an average time constant ranging from 3 to 7 ps; in neutral 50 Å TOP/TOPO-capped InP

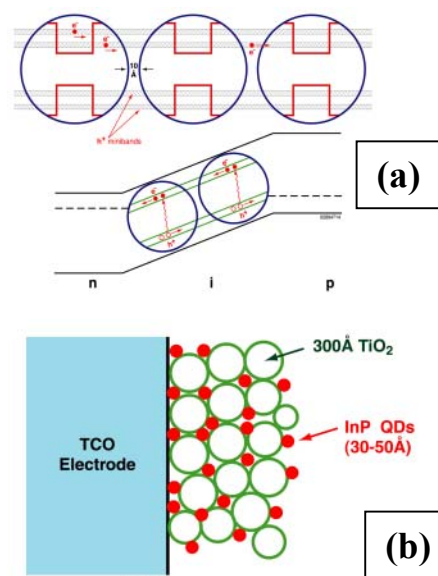QDs, the relaxation shows a large 400 fs component

Figure 3. Configurations for quantum dot solar cells. (A) a QD array used as a photoelectrode for a photoelectrochemical or as the i-region of a p-i-n photovoltaic cell; (B) QDs used to sensitize a nanocrystalline film of a wide bandgap oxide semiconductor (viz. TiO₂) to visible light. This configuration is analogous to the dye-sensitized solar cell where the dye is replaced by QDs; (C) QDs dispersed in a blend of electron- and hole-conducting polymers. In configurations A, B, C, the occurrence of impact ionization could produce higher photocurrents and higher conversion efficiency. In A, enhanced efficiency could be achieved either through impact ionization or hot carrier transport through the minibands of the QD array resulting in a higher photopotential.

indicative of fast electron cooling. These experiments confirm that in the absence of a core-confined hole, electronic relaxation is slowed by about an order of magnitude. A summary of the results of these experiments investigating the effects of electron-hole separation on electron cooling is shown in Fig. 2.

3. Quantum Dot Solar Cells

The two fundamental pathways for enhancing the conversion efficiency (increased photovoltage [3, 4] or increased photocurrent [5, 6] can be accessed, in principle, in three different QD solar cell configurations; these configurations are shown in Fig. 3 and they are described below. However, it is emphasized that these potential high efficiency configurations are conceptual, and there is no experimental evidence yet that demonstrates actual enhanced conversion efficiencies in any of these systems.

3.a. Photoelectrodes Composed of Quantum Dot Arrays

In this configuration, the QDs are formed into an ordered 3-D array with inter-QD spacing sufficiently small such that strong electronic coupling occurs and minibands are formed to allow long-range electron transport (see Fig. 3A). The system is a 3-D analog to a 1-D superlattice and the miniband structures formed therein [2]. The delocalized quantized 3-D miniband states could be expected to slow the carrier cooling and permit the transport and collection of hot carriers to produce a higher photopotential. Also, impact ionization might be expected to occur in the QD arrays, enhancing the photocurrent (see Fig. 1). However, hot electron transport/collection and impact ionization cannot occur simultaneously; they are mutually exclusive and only one of these processes can be present in a given system.

3.b. Quantum Dot-Sensitized Nanocrystalline TiO₂ Solar Cells

This configuration is a variation of a recent promising new type of photovoltaic cell that is based on dye-sensitization of nanocrystalline TiO$_2$ layers [27-29]. In this latter PV cell, dye molecules are chemisorbed onto the surface of 10-30 nm-size TiO$_2$ particles that have been sintered into a highly porous nanocrystalline 10-20 μm TiO$_2$ film. Upon photoexcitation of the dye molecules, electrons are very efficiently injected from the excited state of the dye into the conduction band of the TiO$_2$, affecting charge separation and producing a photovoltaic effect. The cell circuit is completed using a non-aqueous redox electrolyte that contains I$^-$/I$_3^-$ and a Pt counter electrode to allow reduction of the adsorbed photooxidized dye back to its initial non-oxidized state (via I$_3^-$ produced at the Pt cathode by reduction of I$^-$).

For the QD-sensitized cell, QDs are substituted for the dye molecules; they can be adsorbed from a colloidal QD solution [30] or produced in-situ [31-34] (see Fig. 3B). Successful PV effects in such cells have been reported for several semiconductor QDs including InP, CdSe, CdS, and PbS [30-34]. Possible advantages of QDs over dye molecules are the tunability of optical properties with size and better heterojunction formation with solid hole conductors. Also, as discussed here, a unique potential

capability of the QD-sensitized solar cell is the production of quantum yields greater than one by impact ionization (inverse Auger effect) [2, 35]. Dye molecules cannot undergo this process. Efficient inverse Auger effects in QD-sensitized solar cells could produce much higher conversion efficiencies than are possible with dye-sensitized solar cells.

3.c. Quantum Dots Dispersed In Organic Semiconductor Polymer Matrices

Recently, photovoltaic effects have been reported in structures consisting of QDs forming junctions with organic semiconductor polymers. In one configuration, a disordered array of CdSe QDs is formed in a hole-conducting polymer—MEH-PPV (poly(2-methoxy, 5-(2'-ethyl)-hexyloxy-p-phenylenevinylene) [36]. Upon photo-excitation of the QDs, the photogenerated holes are injected into the MEH-PPV polymer phase, and are collected via an electrical contact to the polymer phase. The electrons remain in the CdSe QDs and are collected through diffusion and percolation in the nanocrystalline phase to an electrical contact to the QD network. Initial results show relatively low conversion efficiencies [36, 37], but improvements have been reported with rod-like CdSe QD shapes [38] embedded in poly(3-hexylthiophene) (the rod-like shape enhances electron transport through the nanocrystalline QD phase). In another configuration [39], a polycrystalline TiO$_2$ layer is used as the electron conducting phase, and MEH-PPV is used to conduct the holes; the electron and holes are injected into their respective transport mediums upon photoexcitation of the QDs.

A variation of these configurations is to disperse the QDs into a blend of electron and hole-conducting polymers (see Fig. 3C). This scheme is the inverse of light emitting diode structures based on QDs [40-44]. In the PV cell, each type of carrier-transporting polymer would have a selective electrical contact to remove the respective charge carriers. A critical factor for success is to prevent electron-hole recombination at the interfaces of the two polymer blends; prevention of electron-hole recombination is also critical for the other QD configurations mentioned above.

All of the possible QD-organic polymer photovoltaic cell configurations would benefit greatly if the QDs can be coaxed into producing multiple electron-hole pairs by the inverse Auger/impact ionization process [35]. This is also true for all the QD solar cell systems described above. The various cell configurations simply represent different modes of collecting and transporting the photogenerated carriers produced in the QDs.

4. Conclusion

The relaxation dynamics of photoexcited electrons in semiconductor quantum dots can be greatly modified compared to the bulk form of the semiconductor. Specifically, the cooling dynamics of highly energetic (hot) electrons created by absorption of supra-bandgap photons can be slowed by at least one order of magnitude (3–7 ps vs 400–700 fs). This slowed cooling is caused by a so-called "phonon bottleneck" when the energy spacing between quantized levels in the quantum dot is greater than the LO-phonon energy, thus inhibiting hot electron relaxation

(cooling) by electron-phonon interactions. Slowed electron cooling in quantum dots offers the potential to use quantum dots in solar cells to enhance their conversion efficiency. In bulk semiconductors, the hot electrons (and holes) cool so rapidly to the band edges that the excess kinetic energy of the photogenerated carriers is converted to heat and limits the theoretical Shockley-Quiesser thermodynamic conversion efficiency to about 32% (at one sun). Slowed cooling in quantum dots could lead to their use in solar cell configurations wherein impact ionization (the formation of two or more electron-hole pairs per absorbed photon) or hot electron separation, transport, and transfer can become significant, thus producing enhanced photocurrents or photovoltages and corresponding enhanced conversion efficiencies with thermodynamics limits of 66% (one sun). Three configurations for quantum dot solar cells have been described here that would produce either enhanced photocurrent or photovoltage.

REFERENCES

[1] W. Shockley and H. J. Queisser. *J. Appl. Phys.* **32** (1961) 510.

[2] A. J. Nozik. *Annu. Rev. Phys. Chem.* **52** (2001) 193.

[3] R. T. Ross and A. J. Nozik. *J. Appl. Phys.* **53** (1982) 3813.

[4] D. S. Boudreaux, F. Williams, and A. J. Nozik. *J. Appl. Phys.* **51** (1980) 2158.

[5] P. T. Landsberg, H. Nussbaumer, and G. Willeke. *J. Appl. Phys.* **74** (1993) 1451.

[6] S. Kolodinski, J. H. Werner, T. Wittchen, and H. J. Queisser. *Appl. Phys. Lett.* **63** (1993) 2405.

[7] M. A. Green. *Third Generation Photovoltaics.* (Bridge Printery, Sydney) 2001.

[8] A. Luque and A. Marti. *Phys. Rev. Lett.* **78** (1997) 5014.

[9] F. E. Williams and A. J. Nozik. *Nature* **311** (1984) 21.

[10] A. J. Nozik. *Philos. Trans. R. Soc. London. Ser. A* **A295** (1980) 453.

[11] F. Williams and A. J. Nozik. *Nature* **271** (1978) 137.

[12] H. Benisty, C. M. Sotomayor-Torres, and C. Weisbuch. *Phys. Rev. B.* **44** (1991) 10945.

[13] U. Bockelmann and G. Bastard. *Phys. Rev. B* **42** (1990) 8947.

[14] H. Benisty. *Phys. Rev. B* **51** (1995) 13281.

[15] R. J. Ellingson, J. L. Blackburn, P. Yu, G. Rumbles, O. I. Micic, and A. J. Nozik. *J. Phys. Chem.* **106** (2002) 7758.

[16] J. L. Blackburn, R. J. Ellingson, O. I. Micic, and A. J. Nozik. *J. Phys. Chem.* **107** (2003) 102.

[17] R. J. Ellingson, J. L. Blackburn, J. M. Nedeljkovic, G. Rumbles, M. Jones, H. Fu, and A. J. Nozik. *Phys. Rev. B* (2003) in press.

[18] M. Nirmal, B. O. Dabbousi, M. G. Bawendi, J. J. Macklin, J. K. Trautman, T. D. Harris, and L. E. Brus. *Nature* **383** (1996) 802.

[19] A. L. Efros and M. Rosen. *Phys. Rev. Lett.* **78** (1997) 1110.

[20] U. Bockelmann and T. Egeler. *Phys. Rev. B* **46** (1992) 15574.

[21] A. L. Efros, V. A. Kharchenko, and M. Rosen. *Solid State Commun.* **93** (1995) 281.

[22] V. I. Klimov and D. W. McBranch. *Phys. Rev. Lett.* **80** (1998) 4028.

[23] V. I. Klimov, A. A. Mikhailovsky, D. W. McBranch, C. A. Leatherdale, and M. G. Bawendi. *Phys. Rev. B* **61** (2000) R13349.

[24] P. Guyot-Sionnest, M. Shim, C. Matranga, and M. Hines. *Phys. Rev. B.* **60** (1999) R2181.

[25] M. Shim and P. Guyot-Sionnest. *Nature* **407** (2000) 981.

[26] M. Shim, C. Wang, and P. J. Guyot-Sionnest. *J. Phys. Chem.* **105** (2001) 2369.

[27] A. Hagfeldt and M. Grätzel. *Acc. Chem. Res.* **33** (2000) 269.

[28] J. Moser, P. Bonnote, and M. Grätzel. *Coord. Chem. Rev.* **171** (1998) 245.

[29] M. Grätzel. *Prog. Photovoltaics* **8** (2000) 171.

[30] A. Zaban, O. I. Micic, B. A. Gregg, and A. J. Nozik. *Langmuir* **14** (1998) 3153.

[31] R. Vogel and H. Weller. *J. Phys. Chem.* **98** (1994) 3183.

[32] H. Weller. *Ber. Bunsen-Ges. Phys. Chem.* **95** (1991) 1361.

[33] D. Liu and P. V. Kamat. *J. Phys. Chem.* **97** (1993) 10769.

[34] P. Hoyer and R. Könenkamp. *Appl. Phys. Lett.* **66** (1995) 349.

[35] A. J. Nozik. (1997) unpublished manuscript.

[36] N. C. Greenham, X. Peng, and A. P. Alivisatos. *Phys. Rev. B* **54** (1996) 17628.

[37] N. C. Greenham, X. Peng, and A. P. Alivisatos. "A CdSe Nanocrystal/MEH-PPV Polymer Composite Photovoltaic," in *Future Generation Photovoltaic Technologies: First NREL Conference*, R. McConnell, Ed. (Am. Instit. Phys.) 1997, p. 295.

[38] W. U. Huynh, X. Peng, and P. Alivisatos. *Adv. Mater.* **11** (1999) 923.

[39] A. C. Arango, S. A. Carter, and P. J. Brock. *Appl. Phys. Lett.* **74** (1999) 1698.

[40] B. O. Dabbousi, M. G. Bawendi, O. Onitsuka, and M. F. Rubner. *Appl. Phys. Lett.* **66** (1995) 1316.

[41] V. Colvin, M. Schlamp, and A. P. Alivisatos. *Nature* **370** (1994) 354.

[42] M. C. Schlamp, X. Peng, and A. P. Alivisatos. *J. Appl. Phys.* **82** (1997) 5837.

[43] H. Mattoussi, L. H. Radzilowski, B. O. Dabbousi, D. E. Fogg, R. R. Schrock, E. L. Thomas, M. F. Rubner, and M. G. Bawendi. *J. Appl. Phys.* **86** (1999) 4390.

[44] H. Mattoussi, L. H. Radzilowski, B. O. Dabbousi, E. L. Thomas, M. G. Bawendi, and M. F. Rubner. *J. Appl. Phys.* **83** (1998) 7965.